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Interactive comment on “Model studies of volatile diesel exhaust particle formation: organic vapours involved in nucleation and growth?” by L. Pirjola et al.

Anonymous Referee #2

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The scope and content of this manuscript is timely and important and I suggest that the manuscript can be published in ACP after my comments have been carefully addressed and the English has been improved. The main comment I have concerning the quite crude assumption of representing all condensable organic VOCs as one SVOC with thermodynamics properties of adipic acid. At least some sensitivity test needs to be performed where the condensable organic compounds are represented by ELVOCs instead.

Page 3, L7-10 “The major source of diesel particulate mass is the soot mode. These particles, with sizes of 40–100 nm, are formed in the combustion process and are

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composed of non-volatile carbonaceous soot agglomerates, onto which semivolatile vapours can condense (e.g. Kittelson, 1998; Tobias et al., 2001)."

What do you mean with "size of 40-100 nm"? You need to specify this. Is it mobility diameter? If it is mobility diameter they seem to be quite small for a mass-mode. In figure 7 it seems as if most of soot mass is present above 100 nm in mobility diameter.

Page 3, L16-20: "The GSA has a very low saturation vapour pressure, and it has been shown to participate in condensation and nucleation processes during the dilution and cooling of the exhaust (Arnold et al., 2006, 2012; Rönkkö et al., 2013; Shi and Harrison, 1999; Tobias et al., 2001; Schneider et al., 2005; Khalek et al., 2003). These nucleation mode particles are volatile consisting of sulphate and hydrocarbons (Kittelson, 1998)."

These statements are somewhat contradictory. First you write that GSA has a very low saturation vapour pressure and that it is involved in the formation and growth of NUP but then you write that these particles are volatile. What do you mean with volatile and very low saturation vapour pressure? Is it the sulfuric acid particle volume fraction that is volatile or the hydrocarbon volume fraction and during which conditions are they volatile? Yes, I agree that GSA has a very low saturation vapour pressure in the presence of water in the particle phase. Maybe sulfuric acid evaporates from the NUP if you heat them in a TD? Is this what you mean when you write that the particles are volatile?

Page 5, L10-13: "The main objective of this paper is to quantify the relevant nucleation mechanism and the concentration of a semi-volatile condensable organic vapour (COV) to explain the diesel particle evolution in an ageing chamber under laboratory conditions which mimic well the atmospheric dilution conditions."

In reality I expect that there are thousands of different low and semi-volatile condensable organic vapours that contributes to the particle evolution but you write "a semi-volatile condensable vapour". What do you mean with a "semi-volatile condensable vapour"? If the aim is to develop a 1-product SVOC model parameterization that can

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represent the formation and growth of NUP this should be written clearly. As the main objective is formulated now it is not clear to me if you mean an actual measurable SVOC compound or a model compound which is used to represent VOCs in the exhausts.

Page 8, L15-17: “Condensable organic vapours (COV) are not yet identified, however, the CIMS results indicated that a good candidate might be adipic acid although its concentration could not be accurately measured.”

Change to e.g.: “The condensable organic vapours (VOC) in the diesel exhausts were not identified, however,

What do you mean by “indicated that a good candidate might be adipic acid although its concentration could not be accurately measured.”? Could you explain why the adipic acid could not be measured accurately and why you then still believe that the adipic acid is a good candidate? Maybe you could provide a figure with an example of the measured adipic acid concentration in the supplementary material.

Page 8, L17-20: “We have used adipic acid as a representative of all COVs. Besides condensation, adipic acid was also assumed to participate in heteromolecular nucleation. The thermodynamical properties of adipic acid were adopted from the literature (Bilde et al., 2003).”

So is it correct that you used values of surface tension, mass accommodation coefficient and the vapour pressure of adipic acid from Bilde et al., 2003? Since I expect that these values are crucial for the model results I suggest that you also provide them in the text. I also wonder which surface tension you used for sulfuric acid and if you used the Kelvin effect down to 1.5 nm in diameter or some other theory e.g. Nano-Köhler theory.

Page 8, L27-28: “To minimise the effect of numerical diffusion, typical for sectional models, 100 size sections turned out to be sufficient.” Which sectional approach was used to represent the growth of the particles? Full-moving, full-stationary, moving-

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center ...?

Page 8, L21-23: "In this study, 120 size bins were used to represent the aerosol size distribution ranging from 1.5nm to 10 μ m diameter. Effective density of 1200 kg m⁻³ (Virtanen et al., 2002) was used for soot particles"

Did you use 120 size bins in the MAFOR and 100 size bins in AEROFOR? On page 22, L3-6 you write "The aerosol dynamics models used in this work are process models that describe the main aerosol processes in details. They use sectional representations for particle size distributions with 100 size sections to prevent numerical diffusion and are free from assumptions of lognormal particle modes that are used in modal models."

It seem to be quite crude to use a fixed effective density of the soot particles. See e.g. Fig. 5 from Park et al., Environ. Sci. Technol. 2003, 37, 577-583. But maybe the model results are not very sensitive to the particle density?

On page 7, L26 you write that you take into account wall losses according to Voutsis et al., (2005). Do you then mean both wall losses of particles and gases? Voutsis et al., (2005) refer to Williams and Loyalka (1991) for their wall loss calculations. I suggest you refer to this article too. According to Williams and Loyalka (1991) the deposition velocity depend on Reynolds number. What Reynolds number did you use for the wall loss calculations? Are the model results sensitive to the wall losses?

Page 11, L3-6: "The history of the after-treatment system (ATS) had a large effect on the concentrations, especially, during the first 100% engine load the increasing trend in the GSA concentration indicates strong storage effect of sulphuric acid.", and on Page 14, L21-23 you write "The obtained coefficients A and K vary strongly as a function of the initial GSA concentration. This indicates that nucleation is affected by some other factors than the sulphuric acid concentration."

When I read this I also wonder if SA on the walls of the ageing chamber can influence the nucleation rate. If SA is re-evaporating from the walls it may be important when the

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raw exhaust GSA concentration was low. Could this improve the agreement between the model and measured particle number concentrations for the simulations where only SA is involved in the nucleation process?

Page 14, L4-6: What do you mean with this sentence? “It is not expected that the activation coefficient A was not constant but varied in the range of $2.5 \times 10^{-5} - 2 \times 10^{-1} \text{ s}^{-1}$ as the initial GSA concentration varied from 2.8×10^9 to $2 \times 10^{12} \text{ cm}^{-3}$ (Table 2).” Do you mean that if SA activation nucleation was the actual nucleation mechanism A should be constant?

Page 15, Eq. 4: Did you use the model results from the kinetic nucleation simulations to parameterize the heteromolecular nucleation mechanism coefficients? If this is the case. Please explain this in the text.

Page 16, L10-12: “Hygroscopic properties of COV in MAFOR are that of sodium succinate (Peng and Chan, 2001) with a growth factor of 1.85 at $\text{RH} > 48 \%$ ” Do you mean that it start to take up water at $\text{RH} > 48\%$ and has a growth factor of 1.85 at 90 % RH?

Page 16, L15-19: “An additional non-hygroscopic condensing organic vapour ELVOC with saturation vapour pressure of C34H17 ($p_0(298 \text{ K}) = 5.0 \times 10^{-11} \text{ Pa}$, Lemmon and Goodwin, 2000) was added in the MAFOR simulations to compensate for the initially lower hygroscopic growth and to promote NUP growth to measured size. This should be explained in the method Section 2.2 and not in the results part. I don’t really understand why ELVOCs was need in MAFOR but not in AEROFOR. In reality I would expect that ELVOCs are important at least for the initial growth of the clusters and should be considered in both models. I suggest that you perform some sensitivity test where you instead of using adipic acid use and ELVOC compound to simulate the growth of the particles.

Minor corrections:

Abstract L19-21: “On the other hand, NUP formation was ceased if the GSA concentra-

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tion was less than 10^{10} cm^{-3} which suggests, based on the measurements, the usage of biofuel to prevent volatile particles in diesel exhaust.”

I would reformulate this sentence slightly to: “On the other hand, NUP formation ceased if the GSA concentration was less than 10^{10} cm^{-3} , which suggests, based on the measurements, that the usage of biofuel prevent volatile particles in diesel exhaust.”

Abstract L2: I would replace “during” with “when”.

Page 4, L5-6: “Because vehicle exhaust includes similar species than the atmosphere, NUP formation might occur in the same way.”

Replace “than” with “as in”

Figure 2 need to be saved with higher resolution and all data points should be explained.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4219, 2015.

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